Vibrational Spectral Studies on Biologically Active Complexes of Zinc-II with Benzimidazole

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Abstract- The present study focuses on the synthesis, characterization, and vibrational spectral investigation of biologically active Zinc (II) complexes derived from benzimidazole-based ligands. Zinc (II), an essential trace element with significant biological relevance, forms stable coordination compounds that exhibit diverse pharmacological activities. The synthesized complexes were characterized using elemental analysis, molar conductance measurements, and spectroscopic techniques including Fourier Transform Infrared (FT-IR) and Raman spectroscopy. Detailed vibrational spectral analysis was performed to identify the coordination sites and elucidate the bonding interactions between the Zinc (II) ion and the benzimidazole ligand.

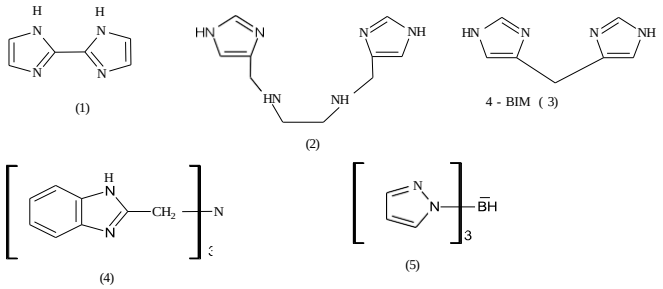
Keywords: Vibrational Spectroscopy, FT-IR Spectroscopy, Raman Spectroscopy, Biological study

Introduction:

Extensive studies on various carbonic anhydrases and alkaline phosphatases have revealed the presence of a catalytic Zn^{2+} ion coordinated to three imidazole residues of histidine in the enzyme active site. In carboxypeptidases and thermolysin, the essential Zn^{2+} ion is coordinated by two imidazole groups and one carboxylate group of the protein. Despite the considerable interest in such biologically important systems, relatively few chelating ligands containing imidazole rings have been synthesized, and none have combined three simple imidazole rings as models for the metal-binding sites of carbonic anhydrase.

The synthesis reported by Fruton from histidine is not readily adaptable for the preparation of related tris(imidazole) ligands. Thompson et al. have described the metal-binding properties of a tris (benzimidazole) ligand system. Another related ligand class is the tris(pyrazolyl) borohydride system, first reported by Trofimenko and subsequently investigated in detail by Marks and Ibers.

X-ray crystallographic studies of carbonic anhydrase have shown that the three imidazole ligands adopt a distorted tetrahedral coordination geometry around the Zn^{2+} ion. Molecular modeling studies suggest that a similar geometry can be achieved using tris(imidazolyl)methane derivatives, making them attractive structural models for zinc-containing metalloenzyme active sites.



Benzimidazole complexes of transition metals have attracted considerable attention because of their interesting spectral, magnetic, and biological properties. The oxime functional group, when located adjacent to another donor atom within an organic molecule, acts as an effective chelating moiety and enhances the ligand's ability to coordinate with metal ions. Such ligands have found wide applications in the separation, detection, and estimation of metal ions owing to their strong metal-binding capabilities.

In the present study, the synthesis and characterization of Zinc (II) complexes derived from 2-acetyl-4-methylbenzimidazole oxime ($ACMBZOXH_2$) and 2-benzoyl-4-methylbenzimidazole oxime ($BzMBZOXH_2$) are reported. The complexes were investigated using vibrational spectral techniques to elucidate their coordination modes, bonding characteristics, and structural features.

Experimental:

Material and Methods: The chemicals used were of AR or equivalent purity, 4−Methyl−2−Acetyl benzimidazole and 4−methyl−2−benzoyl benzimidazole were prepared by the reported methods.[12] Their oximes were prepared by refluxing the ketone and hydroxylamine hydrochloride in ethanol in presence of pyridine. The excess of ethanol was removed by distillation or evaporation oximes were purified by recrystallisation from methanol−benzene mixture.

Synthesis of Complexes: To an ethanolic solution of 2−Acetyl benzimidazole oxime (0.005 ol), metal (II) chloride/nitrate/sulphate (0.005 mol) in the same solvent or metal (II) acetate in water was added. The resulting mixture was refluxed on a water bath for 2−hour cooled and filtered, washed with ethanol and dried over phosphorous pentoxide.

In the synthesis of 4−methyl−2−benzoyl benzimidazole oxime complexes, the ligand (0.005 mol) was dissolved in the minimum quantity of ethanol and metal (II) chloride/acetate (0.005 mol) in water was added. The resulting precipitate was refluxed on a water bath for 2−hour cooled, filtered and washed with aqueous ethanol and dried, over phosphorous pentoxide.

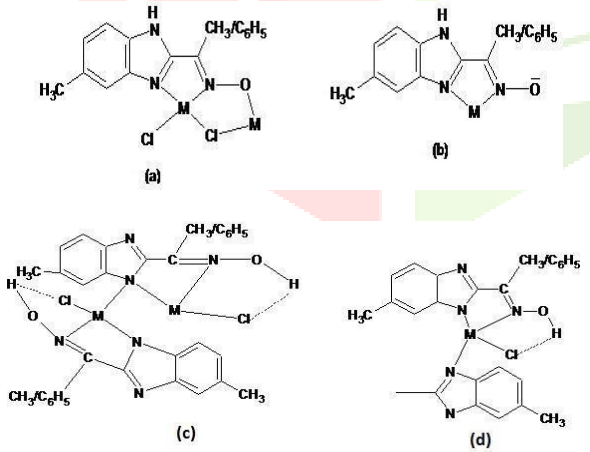
Results and Discussion: The elemental analysis of the complexes along with their magnetic moment data are given in table-1. The complexes are insoluble in common organic solvents except in DMF, DMSO and pyridine. The molar conductances of 10^{-3}M DMF−solutions of the complexes were found to be in the range 7−30 mho cm^2 mol^{-1}. The slightly higher values than those of expected for non-electrolytes indicate the solvation of the complexes resulting in the displacement of anion from coordination sphere by

strong donor DMF molecules. The complexes may be regarded as non electrolytes.

Magnetic Properties: The Zinc(II) complexes $[Zn(C_{10}H_{10}N_3O)]Cl$ and $[Zn(C_{10}H_{10}N_3O)_2]2H_2O$ show moment values of 3.95 and 4.02 B.M. respectively. These are much lower than the values expected for tetrahedral (4.2 − 4.7 B.M.) or octahedral (4.7 − 5.2 B.M.) Zinc (II) complexes. This lowering of magnetic moment may be explained by assuming the co−existence of high spin as well as low spin states of Zn(II) ($t_{2g}^5 e_g^2 \rightleftharpoons t_{2g}^6 e_g^1$) the presence of ant ferromagnetism or the polymeric nature of the complexes. The □+effective value of $[Zn(C_{15}H_{12}N_3O)_2].2H_2O$ (4.90 B.M.) agrees very well with the expected value for octahedral Zinc(II).

Ultervoilet Spectra: The electronic spectra of $[Zn(C_{10}H_{10}N_3O)]Cl$ showed a multicomponent band at 14815 cm^{-1} which is typical of a tetrahedral Zinc (II) complex. This is assigned to ν_3−band resulting from $^4T_1(P) \leftarrow {}^4A_2$ transition. The band observed at 6896 cm^{-1} may be taken as ν_2 band $^4T_1(F) \leftarrow {}^4A_2$. The spectrum of $[Zn(C_{10}H_{10}N_3O)_2]2H_2O$ was quite different from that of $[Zn(C_{10}H_{10}N_3O)]Cl$ and showed two bands at 20490 and 7145 cm^{-1}. These are assigned to the transitions $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ and $^4T_{2g} \leftarrow {}^4T_{1g}(F)$ respectively of octahedral Zn(II) complex. The ν_2− band, since it involves a two electron transition was not observed. Its position was calculated using konig equation. The various ligand field parameters (Dq, B □, □, ν_2/ν_1 and LFSE) have been calculated. The ν_2/ν_1 ratio for $[Zn(C_{10}H_{10}N_3O)_2].2H_2O$ is found to be in the range (2.1 −2.2) which is reported for octahedral Zinc(II) complexes. Satisfactory electronic spectrum could not be obtained for $[Zn(C_{15}H_{12}N_3O)_2].2H_2O$.

Vibrational Spectra: A comparison of the infrared spectra of the ligands and their complexes indicated that the benzimidazole oximes were coordinated to the metal in the present complexes in four different ways (a − d)



In type (b) $[Zn(C_{10}H_{10}N_3O)_2].2H_2O$ and $[Zn(C_{15}H_{12}N_3O)_2].2H_2O$ complexes, the ligands behave in a mono basic bidentate manner coordinating through the oxime nitrogen and tertiary imidazole nitrogen. The NOH group is deprotonated as shown by the disappearance of the ligand band at 3250−3280 cm^{-1}. A band at 3360−3450 cm^{-1} is assigned to ν(OH) of coordinated water. The coordination through oxime nitrogen and tertiary nitrogen is suggested from the lowering of ν(C=N) as in type (a) complexes.

In type (c) $[Zn(C_{10}H_{10}N_3O)]Cl$ complex the ligand behaves as a monobasic tridentate ligand coordinating through the oxime nitrogen, pyrrole nitrogen and tertiary nitrogen of imidazole moiety thus forming a polymeric complex N(OH) of oxime function is observed at 3240 cm^{-1} due to hydrogen bonding with chloride. ν(NH) Disappears confirming deprotonation and coordination through the nitrogen. The coordination through oxime nitrogen and tertiary nitrogen is suggested by the lowering of ν(C=N), ν(N−O) in the ligands assigned of 935−950 cm^{-1} shifts to higher frequency as a result of coordination through oxime nitrogen.

Conclusion:

In conclusion, we have widened a practical and novel procedure for the selective synthesis of Zinc (II) complexes [Zn(C10H10N3O)]Cl and [Zn(C10H10N3O)2]2H2O by using Infrared and electronic spectra. The present procedure has a several advantage, mild reaction, non harzadous methed, experimental easy and simple workup process, less reaction time to conventional method

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Table-1: Analytical Data of the Complexes

S. No.	Complex	Colour	% Chemical Analysis Found (Calculated)					□−effective (B.M.)
			C	H	N	M	Anion	
1.	[Zn ($C_{10}H_{10}N_3O$)]Cl	Red	42.38 (4.48)	3.40 (3.54)	14.70 (14.87)	20.72 (20.86)	2.41 (2.56)	3.95
2.	[Zn ($C_{10}H_{10}N_3O)_2$]$2H_2O$	Pink	50.80 (50.96)	4.90 (5.09)	17.70 (17.83)	12.40(12.51)	–	4.02
3.	[Zn ($C_{15}H_{12}N_3O)_2$]$2H_2O$	Red	64.30 (64.40)	4.88 (5.0)	14.90 (15.02)	10.40(10.54)	–	4.90

Table-2: Electronic Spectral data and ligand field parameters of the complexes

S.No.	Complex	□−max (cm^{-1})			Dq (cm^{-1})	B (cm^{-1})	□	v_2/v_1	LFSE (Kcal mol^{-1})
1.	[Zn ($C_{10}H_{10}N_3O$)]Cl	6898	14820		404	645.3	0.662	–	13.8
2.	[Zn ($C_{10}H_{10}N_3O)_2$]$2H_2O$	7145	15380	20494*	825	963.6	0.992	2.15	18.9
3.	[Zn ($C_{15}H_{12}N_3O)_2$]$2H_2O$	7830			–	–	–	–	–

Table-3: Infrared Spectral Data (cm^{-1}) of complexes

S. No	Compounds	ν(OH) water	ν(OH) oxime	ν(NH)	ν(C=N) oxime	ν(C=N) imidazole	ν(C=C)		ν(M−N)	ν(M−O)	ν(M−Cl)
Ligands											
1.	4−methyl−2−Acetyl benzimidazole oxime (MACBZOXH$_2$)	–	3280	3160	1625	1570	1520	935	–	–	–
2.	4−methyl−2−benzoyl benzimidazole oxime (MBZBZOXH$_2$)	–	3250	3140	1620	1580	1540	950	–	–	–
Complexes											
3.	[Zn ($C_{10}H_{10}N_3O$)]Cl	–	3240	–	1600	–	1545	1010	445	–	300
4.	[Zn ($C_{10}H_{10}N_3O)_2$]$2H_2O$	3420	–	3200	1600	–	1540	980	420	385	–
5.	[Zn ($C_{15}H_{12}N_3O)_2$]$2H_2O$	3400	–	3200	1600	–	1550	1020	–	–	–

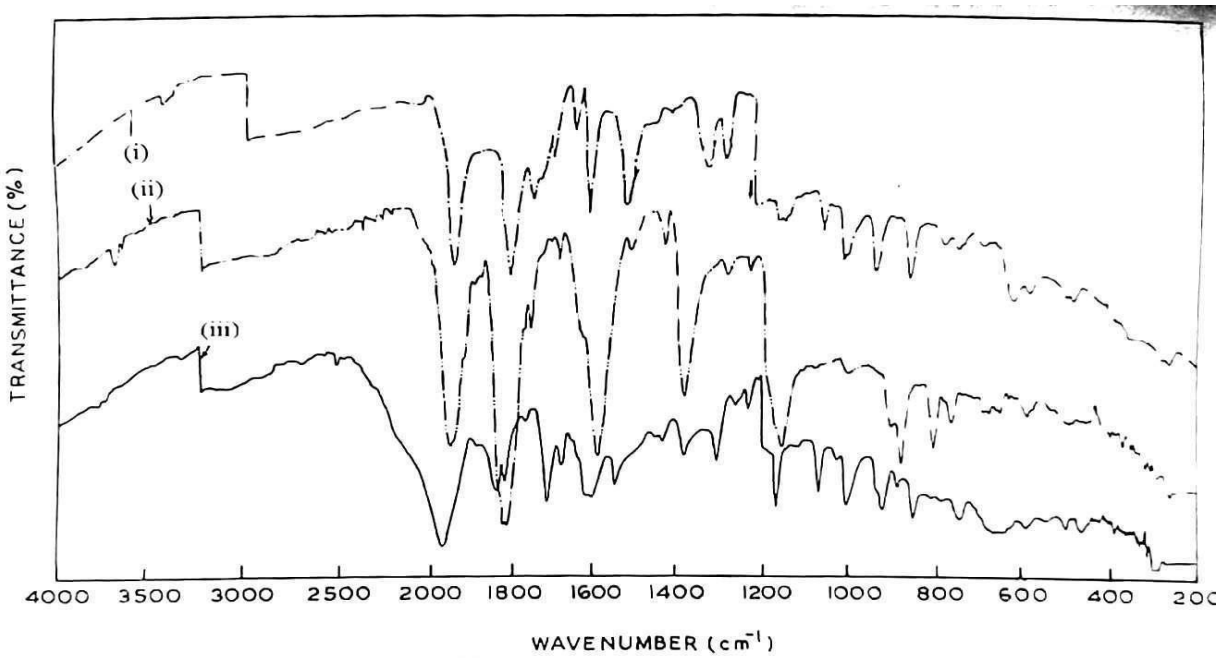

Fig. 1 IR SPECTRA OF COMPLEXES

(i) [[Zn $(C_{20}H_{16}N_6)_2$] I_2 (ii) [Zn $(C_{24}H_{22}N_4)_2$] $(ClO_4)_2$ (iii) Zn Cl_2 $(C_{24}H_{22}N_4)$